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## **Chemical aspects related to using recycled geopolymers as an aggregate**

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## **Chemical aspects related to using recycled geopolymers as an aggregate**

### **Abstract**

Despite extensive research into geopolymers' sustainability, it is deemed essential to investigate largely overlooked end-of-life aspects. This requires investigation of alkalis' leaching potential from the geopolymeric matrix. To study the feasibility of geopolymer concrete (GPC) recyclability, migration of alkalis was evaluated for the first time on a microstructural level through SEM/EDX elemental mapping and leaching tests. Macroscale impacts were assessed by investigation of Portland cement (PC)-mortar properties affected by alkalis concentration. Leaching tests indicated alkalis becoming immediately available in aqueous environments, but the majority remained chemically or physically bound in the matrix. This type of leaching accelerated the initial setting of PC-paste. Elemental mapping and SEM/EDX analysis showed a complex paste-aggregate interfacial transition zone. Exchange of Ca and Na, revealed by the maps, resulted in migration of Na into the PC-paste and formation of additional Ca-Si based phases in the geopolymeric matrix. Strength values of mortars with 25% and 50% recycled aggregates (RA) showed negligible differences compared to the reference. Screening tests indicated low potential for GPC-RA inducing alkali silica reaction. Transport of GPC-RA alkalis and the underlying mechanisms were observed. This phenomenon had minor effects on PC-mortar properties indicating that recycling of geopolymers is a viable reuse practice.

### **Keywords chosen from ICE Publishing list**

Chemical properties, Geopolymers, Recycled material, Chemical properties; Electron microscopy, Leaching

### **List of notation**

<i>ASR</i>	is the alkali silica reaction
<i>BSE</i>	is backscattered electron
<i>C-S-H</i>	is the calcium silicate hydrate
<i>EDX</i>	is the Energy-dispersive X-ray spectroscopy
<i>FA</i>	is the fly ash
<i>GGBS</i>	is the ground granulated blast furnace slag
<i>GPC</i>	is the geopolymer cement
<i>ITZ</i>	is the <i>interfacial transition zone</i>
<i>NA</i>	is the natural aggregates
<i>PC</i>	is the Portland cement (in this study CEMII/BV 32.5R Portland-fly ash cement)
<i>RA</i>	is the recycled aggregates
<i>SEM</i>	is the Scanning Electron Microscopy
$\Delta$	is the Difference

## 1. Introduction

The call for sustainability in construction has lead the cement industry to the investigation of low carbon binders as replacements for Portland cement. Geopolymers were popularized by Joseph Davidovits in the 1970's but have recently returned to the forefront of research due to their reported strong environmental credentials. Geopolymers are manufactured through mixing a solid aluminosilicate with a highly concentrated aqueous alkali hydroxide or alkali silicate solution (Duxson *et al.*, 2007). Amongst the various types, fly ash (FA) / ground granulated blast furnace slag (GGBS) geopolymer cement (GPC) is deemed appropriate for high volume applications such as construction due to its properties, as well as cost and availability of raw materials (Heath *et al.*, 2013; McLellan *et al.*, 2011; Shi and Day, 1999; Li *et al.*, 2013; Kumar *et al.*, 2010; Nath and Sarker, 2014; Gunasekara *et al.*, 2015).

The environmental impact of geopolymer cement manufacturing has been extensively investigated, but little attention has been given to reuse or disposal scenarios (Akbarnezhad *et al.*, 2015) and this information is crucial for accurate and complete Life Cycle Assessment (LCA) analyses. This paper presents part of a project examining the recyclability of FA/GGBS geopolymer paste concretes as an aggregate in new concrete. The specific work presented here is looking at an upper bound where pure geopolymer paste has been processed to sand size and used as an aggregate in new Portland cement based mortars.

The experimental series presented focused on investigating the potential of alkali leaching from the GPC recycled aggregates (RA) into the Portland cement mortars (PC). The hypothesis of alkali contribution from natural aggregates into the paste has been investigated by a number of researchers (Bérubé *et al.*, 2002; Rajabipour *et al.*, 2015). It has been suggested that alkali release from non-reactive aggregates can be large enough to influence the concrete prism test results (Ideker *et al.*, 2010). In a particular study, alkalis on pore fluid were measured by hot water extraction and they were found to exceed the calculated amount (assuming concrete with typical cement content) by 0.25 to 0.30%  $\text{Na}_2\text{O}_{\text{eq}}$  by mass of cement. The difference between the calculated and obtained value was attributed to the aggregates (Rajabipour *et al.*, 2015). The fundamental chemical and physical differences between an amorphous geopolymer matrix and a crystalline natural aggregate mean that this previous work can only be used more as a

guide and not a comparative for the studies carried out in this paper. The geopolymeric matrix is highly alkaline due to the activating solutions and can have a higher porosity than to natural aggregates. This makes it highly possible that incorporation of recycled geopolymer as aggregates in new mixes will result to a significant increase of the overall alkalinity of the paste which can affect a number of fresh and hardened properties.

Water soluble alkalis from aggregates could diffuse almost immediately into the aqueous phase of the paste during the mixing if they are available and there is sufficient mix water for dissolution. Some alkalis in the recycled paste are likely to be bound into solid phases and potentially be unavailable to the mix water. Alkalis present in the fresh paste can either be incorporated into the C-S-H gel or become concentrated into the aqueous phase and remain present in the pore fluid (Hong and Glasser, 1999; Myers *et al.*, 2015; Jawed and Skalny, 1978). The findings about the capacity of alkali uptake from C-S-H are variable but there is a consensus regarding the factors affecting it. The underlying governing mechanisms are related to charge balancing processes and the overall incorporation depends on initial concentration of alkalis in the aqueous solution, the Ca: Si ratio of the paste and the presence of aluminum in the precursor (Hong and Glasser, 1999; Myers *et al.*, 2015). The high pH of the cement pore fluid though, reported by a number of authors, provides strong evidence that a significant number of alkalis remain in the aqueous medium (Jawed and Skalny, 1978; Taylor, 1987; Buckley *et al.*, 2007; Kim *et al.*, 2015; Rajabipour *et al.*, 2015)

The second situation could increase the potential of alkali silica reaction (ASR) occurrence in PC elements incorporating GPC RA, because pore fluid is the medium bringing alkalis in contact with the amorphous silica of aggregates (Rajabipour *et al.*, 2015; Chatterji, 2005) .

Another implication of potentially water soluble alkalis, is that their presence in the aqueous phase affects the hydration processes of cement. The solubility of Ca or  $\text{Ca(OH)}_2$  is suppressed the presence of alkalis (Hong and Glasser, 1999; Jawed and Skalny, 1978). On the contrary, Si solubility increases with increasing alkali concentration. This, along with other interactions, results in alteration of hydration kinetics, growth, microstructure and morphology of hydration products. Distinct effects of alkalis in cement are the crystallization of C-S-H, acceleration of

setting, increase of early and reduction of final strength (Jawed and Skalny, 1978; Mota Gassó, 2015).

## 2. Materials

A geopolymer paste was used as the parent material for the recycled aggregates (RA). This was done to investigate an upper bound of geopolymer paste and provide a simplified matrix system without influence of parameters such as aggregates or impurities. PC mortars with 0%, 25% and 50% replacement (by mass) of natural aggregates (NA) by GPC RA were cast. The test results for GPC recycled aggregates were evaluated against PC recycled aggregates and natural sand.

**Table 1 Mix design for mortars with recycled aggregates**

Materials in kg/m <sup>3</sup>					
Sample ID	PC	NA	PC RA	GPC RA	Water
PC_100%NA	960	2160	-	-	451
PC_25%PC	960	1620	540	-	451
PC_50%PC	960	1080	1080	-	451
PC_25%GPC	960	1620	-	540	451
PC_50%GPC	960	1080	-	1080	451

For the geopolymer precursor, GGBS (procured by Hanson Heidelberg cement group from the Port Talbot works) and FA (CEMEX 450-S, BS EN 450-1 Fineness Category S; LOI Category B) were used. The chemical composition of the precursors as obtained by X-ray fluorescence is presented in Table 2. For the activating solution, NaOH pellets (>98% purity) were mixed with distilled water and sodium silicate powder with Na<sub>2</sub>O~27.0%, SiO<sub>2</sub>~53.5%. The chemicals were both supplied by Sigma-Aldrich.

**Table 2 Chemical analysis of precursors by X-Ray fluorescence**

Constituents (wt%)	GGBS	FA
SiO <sub>2</sub>	35.15	49
Al <sub>2</sub> O <sub>3</sub>	13.07	23.5
Fe <sub>2</sub> O <sub>3</sub>	0.28	8.7



CaO	39.6	2.4
MgO	8.47	1.4
SO <sub>3</sub>	0.17	0.8
Na <sub>2</sub> O	0.14	3.06
K <sub>2</sub> O	0.51	0.87
TiO <sub>2</sub>	0.66	
MnO	0.44	
P <sub>2</sub> O <sub>5</sub>		1.1
LOI	0.97	4.4

For each batch of geopolymer paste, 10 kg of precursor with fly ash to GGBS ratio 1:1 were used. The corresponding activator was 906gr of sodium silicate solution mixed with 330g NaOH and 2.375 litres of distilled water. The total Na calculated as Na<sub>2</sub>O% equivalent per mass of precursor was 5% which is a level that was expected to result in some excess (unbound) alkalis. The activator solution was left to cool for 24 hours prior to mixing as the exothermic dissolution increased the temperature of the solution. For the PC recycled aggregates, paste with water to cement ratio 0.5 was cast. For all PC elements, a low alkalinity Portland-fly ash cement was used. (Sulfacrete EN 197-1 –CEMII/BV 32,5R supplied by Tarmac Cement & Lime Ltd, LOI of fly ash <7%, minimum fly ash ~25%). Standard sand complying with BS EN 196-1 was used as natural aggregate.

The pastes for the recycled aggregates were cast in cubes of 100mm at the laboratory. They were cured for 28 days in sealed plastic bags at ambient temperature and then crushed according to BS 12390-3 to determine compressive strength. The mean strength values were 45.5 MPa and 47.8 MPa for PC and GPC paste correspondingly. The recycled pastes were designed to have equivalent strength in order to provide comparable results. The pieces were put through a rock crusher with the jaws' opening set at 1mm. It was then sieved and rebleded to the similar particle size distribution as the standard sand complying with BS EN 196-1. The final RA product was a sand with equal percentages of particle sizes 2-1mm, 0.5-1mm and 0.5-0mm.

### 3. Methods

An extraction test to determine water-solubility of alkalis and other compounds of the geopolymer aggregates was conducted. The procedure was based on the one described in BS EN 1744-6 for the duration and method of extraction. The recommendations of BS EN 1744-1 were followed for the liquid to solids ratio. Aggregate test portions were mixed with demineralised water at a 1:1 water to solids ratio. Two extractions were carried out in parallel, for a total of 3 hours with agitation by turning every 30 minutes. The pH of the extracts was measured just before the agitation took place at 30 minute intervals. At the end of the immersion period, the extract was filtered and used per the procedures of BS EN 1744-6 and as described later.

The influence of the recycled aggregate extract on the initial setting time of cement was evaluated according to BS EN 1744-6. For this test, the initial setting of a standard consistency CEMI paste made with demineralised water was measured using the Vicat equipment. Then, following the same the initial setting time of a paste made with the recycled aggregate extract was determined. The influence on the setting time due to the aggregate extract was calculated.

The GPC aggregate was subjected to energy dispersive x-ray (EDX) scanning electron microscopy (SEM) analysis before and after the extraction and the obtained spectra were compared to identify leaching of elements. Crushed uncoated sample was placed on a carbon tape. The aggregate samples were examined at low, medium and high magnifications. The element used for optimization of spectrum was copper. A threshold of 1 sigma was set and all qualitative results below that, have been set to zero. The data were recorded as atomic percentage of element in the examined area (atomic %).

Backscatter electron (BSE) imaging and EDX/SEM elemental mapping was also conducted on 6 month old mortars. The purpose of this was to investigate whether alkalis are transferred to the PC matrix and to attempt to determine the mechanism through which the transfer took place. It was considered possible that if alkalis are easily soluble in water, the transfer would take place during mixing. If any transfer would take place at later age it would most probably be through

the interfacial transition zone (ITZ). This hypothesis can easily be tested by elemental mapping as any patterns of sodium leaching from the GPC aggregate into the paste would be apparent.

Cubic pieces with 20mm edge and 10mm depth were cut from mortar prisms, cast into low viscosity epoxy resin and then polished to reveal the top surface of the specimens. The EDX was conducted at low vacuum mode, at pressure of 30 Pa. The time for the element mapping varied from 35 to 45 minutes. Results below 2 sigma were set to zero.

For all SEM EDX analyses, a JEOL JSM-6480LV SEM with Oxford Instruments X-Act EDX detector was used with accelerating voltage 20 kV and process time 5s.

The potential for alkali silica reaction was investigated according to “Accelerated Mortar bar method” as described in ASTM C1260-14 (the procedure is identical to that described in the withdrawn British DD 249:1999) which is the appropriate test for the fine aggregates used in this study). The test was conducted on 4 mortar bars of 25mm x 25mm x 250mm with studs in the longitudinal direction. The bars were kept at 80°C for the whole duration of the test; in water for 1 day after demoulding, then in 1M NaOH solution for 14 days. The total length change after the 14 day immersion period is the criterion to identify alkali silica reaction occurrence. For mean expansion value higher than 0.10%, formation of alkali-silica gel is considered possible and further investigation is required.

Additionally, the 28 day compressive strength of the mortars incorporating RA was tested according to the procedure described in BS EN 1015-11.

## **4. Results and discussion**

### **4.1. GPC-RA extraction**

The alkalinity of the water increased immediately after the GPC RA immersion, rising from approximately pH=7 to higher than pH=12. This is approximately a 39% increase of the pH value, which corresponds to a rise in OH<sup>-</sup> concentration from 6.3x10<sup>-7</sup> to 3.1 x10<sup>-2</sup> mol/l. A slight and steady increase took place for the first 2 hours and after that the values appear to stabilise as indicated by Figure 1. The duration of the test was short compared to standard leaching tests

in order to better replicate the situation where recycled aggregates are combined with mix water. Therefore, the observations were more likely to relate to short term processes such as dissolution or washout, rather than provide information for the diffusion mechanism of Na through the geopolymeric paste. The sharp pH increase though was indicative of alkalis which are water-soluble and could become immediately available during mixing of mortar or concrete. The total amount of Na<sub>2</sub>O from the precursors and activators in 1 kg of the recycled aggregate is approximately 66 g. If all of this leached in 1 litre of water during the extraction process, the concentration of Na<sub>2</sub>O in the water would be just over 1 mol /l. Although sodium will not be in the form of Na<sub>2</sub>O in the aqueous solution, it does indicate that this level of soluble sodium will not result in an OH<sup>-</sup> concentration of only 3.1 x10<sup>-2</sup> mol /l as indicated by the pH. Therefore, it can be concluded that the majority of Na<sub>2</sub>O is not available for dissolution during the time period of the leaching test. This is most likely because of a combination of chemical and physical bonding.

This was confirmed by SEM-EDX measurements which were taken to determine the atomic concentration in the mixes before and after 3 hours of leaching. SEM/EDX measurements were also taken from an additional sample which was subjected to extended, 5 day leaching. Fourteen different sites were used before leaching, and seven after leaching, and, as shown later in spectral maps, there is considerable variation in Na concentration within samples. The EDX spectra indicated a broad range in Na concentrations which makes it difficult to conclusively determine how much the Na<sub>2</sub>O concentration had reduced. An ANOVA analysis of the data indicates that at the 95% confidence level, it is not possible to determine if there is a significant difference in the overall Na concentration in the recycled aggregate before or after leaching. This demonstrates that the increase in pH in the leachate water is probably a better indicator of available alkalis than the decrease in concentration in the recycled aggregate. The leaching test is, however, not the true representation of the mix process that the elemental maps represent as an actual mix situation has water available for leaching alkalis influenced by hydration reactions and vice versa. It should be noted that as the quantity of Na far exceeded the quantity of K in the mix, therefore the movement of the Na was the focus of this investigation.

In addition to Na, other elements may have leached from the recycled aggregates and influenced hydration products, but this were also not clearly discernible from the EDX spectra. This effect of leached elements on the hydration products was not directly examined in the present paper, but the indirect effects were examined through the set-time, compressive strength and BSE/SEM images.

#### **4.2. Elemental maps of mortars**

After the solubility of Na from GPC RA was confirmed, elemental mapping was performed on the final mortars. The mapping had two purposes: the first one was to visually examine the distribution of sodium in the PC mortar paste to determine whether this was uniform or concentrated at the interface between the PC paste and the GPC RA. The second was a semi quantitative analysis to estimate how the GPC RA affects the overall Na concentration in the paste, compared to the samples with PC RA and natural aggregates (NA).

Each pixel of the elemental map is defined by a spectrum with known coordinates. The spectrum provides information about the detected elements, in terms of atomic percentages. The values for a single spectrum are normalised to 100% by the analysis software (INCA). Using this information INCA derives the highest and lowest percentage for every element detected on the mapped area. These values are presented using the terms “Max” and “Min percent”. Additionally, INCA generates the “Sum spectrum”, which is the average value of the atomic percentages for a single element. The Sum spectra for a single map are normalised to 100% and provide information about the average concentration of each element at the examined area. Due to the averaging and normalisation, the presence of areas with high concentration on a specific element can result to high values which are not characteristic of the whole map. For example, in Figure 4 the presence of NA increases the Sum spectrum of Si in relation to values of other elements. Although, the mapped areas were chosen to provide representative results, the effect is inevitable in locations of interest with GPC RA such as those presented in Figures 3-7. To

reinforce the results, individual spectra from the paste of the mapped areas were taken. The average of Na percentages was calculated and is presented with the term "Paste average". All the results were normalised to the Sum spectrum of the reference mix OPC\_100%NA and are represented graphically in Figure 2.

Although the data is quantitative, it should be considered in a qualitative manner as the sample size is small compared to the aggregate dimensions and the trends are better illustrated in the BSE/SEM images later. As expected, the Sum spectra of the mortars with GPC RA showed higher Na content than all other mixes but the variability between samples showed that higher GPC replacement did not result to proportionally overall higher Na content. The samples with the recycled PC aggregate also showed an increased Na content in comparison to the NA sample. PC RA have higher Na content compared to the standard sand used in the present study. When a proportion of the sand is replaced by PC RA, the cumulative amount of Na in the mortars was expected to be higher compared to that of the reference mix. However, the data of paste average in Figure 2 does indicate that as expected, the Na concentration is likely to be more of a concern when using recycled geopolymer aggregate. Specifically, the paste averages for mortars with 50% and 25% GPC RA are 5% and 4% higher compared to the sum spectrum of the reference mix. In the case of mortars with PC RA the corresponding values present a relative increase of 1.4% and 3% for 25% and 50% PC RA, accordingly. It should be noted that the absence of a column in Figure 2 indicates a recorded value below the threshold or zero. As mentioned earlier and demonstrated in Figures 3-5, the values of Max percent in samples with GPC aggregate and PC paste correspond to the GPC RA areas.

Elemental maps of the mortars incorporating GPC RA are presented in Figures 3 to 7. The pictures present the distribution of Ca and Na along with the SEM images of the examined areas. Ca maps were used to distinguish the PC paste from the GPC RA and were also indicative of the 'border line' between the two materials. The brightness of color is proportional to the element concentration. White indicates high concentration, while grey corresponds to low or zero values.

It is noticeable that in all electron images the two materials presented quite distinct morphologies. In all cases unreacted fly ash spheres are present in both the GPC RA and the PC matrix, visible as circles on the images. Some unreacted GGBS is also visible in the GPC, indicated as a largely straight-sided form with high Ca concentration.

As far as Na is concerned, in Figure 3 a scattered distribution of the element in the paste is shown. A slightly higher concentration was observed at the area corresponding to the GPC RA but the results regarding the PC paste were variable. On the top-middle left side, a continuous concentration beyond the interfacial transition zone (ITZ) was shown. In contrary, on the middle right area of the image Na seemed absent in areas of the PC paste. This continuous distribution was considered as an indication of sodium transfer not only through water but also through the ITZ at later ages. In order to examine this observation further, samples were examined at higher magnifications.

By examining Figures 4 and 5 it became more obvious that Na had been transferred in the PC paste not only through dissolution in water but also by leaching through the ITZ, as there was a gradual decrease in Na concentration past the paste boundary. A relatively high scattered distribution in the paste was confirmed while the leaching through the ITZ zone is apparent in Figure 5. In these higher magnification images, the calcium outline appeared less sharp in comparison to Figure 3. A higher concentration of calcium close to the ITZ zone that cannot be related to GGBS particles was revealed.

In Figures 6 and 7, the effect is more subtle and it appears there was a continuity in the Na dispersion. This low contrast is indicating that the Na concentration was similar between the two materials and it appeared unaltered for at least 100  $\mu\text{m}$  beyond the aggregate-paste interface.

In addition, in Figures 6 and 7, revealed a reverse phenomenon of calcium leaching from the PC paste into the geopolymeric matrix through the ITZ. The concentration of calcium at those points cannot definitely be related to GGBS particles as indicated by the SEM images and the shape of the point. Instead it appeared that these points corresponded to a geopolymeric phase with

quite distinct morphology compared to the rest of the material. Additional spectra of those areas (not presented here) showed high Si and low Al concentration that goes along with the high Ca concentration and this may indicate the formation of a C-S-H type product. The physical appearance of that product seemed to be denser and more homogenous than the rest of the geopolymer material.

A number of researchers report distinct products from fly ash and GGBS alkali activation, with the later resulting to the formation of a denser C-S-H type gel (Chi and Huang, 2013; Li *et al.*, 2013; Ismail *et al.*, 2014; Gunasekara *et al.*, 2015). The phase shown in Figures 6-7 has similar morphology to such gels. However the absence of GGBS particles in the specific location, allows the consideration of the adjacent PC paste as a potential source for Ca.

Substitution of  $\text{Na}^+$  by  $\text{Ca}^{2+}$  in silica networks is considered a plausible mechanism for alkalis exchange during ASR (Rajabipour *et al.*, 2015), while substitution of CaO by  $\text{NaO}_2$  in aluminates and silicates is reported by Jawed and Skalny (Jawed and Skalny, 1978). The latter ones attribute this phenomenon to similar ionic radii of  $\text{Ca}^{2+}$  and  $\text{Na}^+$ , which allows substitution in the crystal matrices without significant alteration of the free energy of the system. Another identified phenomenon was the accumulation of Na on partly or non-reacted fly ash particles. It is noticeable that Ca was largely absent from the fly ash particles as shown in Figures 6 and 7.

Spectra from specific points were taken from PC\_25%GPC Site2 and PC\_50%GPC Site3. The points of interest were located in the paste, close to ITZ (approximately up to 9  $\mu\text{m}$  from the interface) and in the GPC-RA. The average of the Na atomic percentages was calculated and normalised to the average Na percentage of the corresponding GPC RA area of each site. The results are presented in Figure 8 and they indicated the relative Na concentration of the mortar paste close and further from the ITZ. In the case of PC\_50%GPC the gradient of Na concentration was more obvious as the relative percentage changed from approximately 85% close to the ITZ to less than 60% in the paste. On the PC\_25%GPC this transition did not seem to take place as the average Na concentration close to ITZ and further away were almost equal (approximately 60% that of the GPC RA area).

#### **4.3. Mechanical and physical properties**



#### **4.3.1.Initial setting time**

The influence of the aggregate extract in terms of minutes' difference on initial setting times was calculated using equation (1) of BS EN 1744-6.

Two pastes of standard consistency (according to BS EN 196-3) were prepared using 500g of CEMI and 175g of demineralised water and extract. The initial setting times, determined using a manual Vicat equipment, showed the aggregate extract to cause acceleration of 13 minutes. This accelerating effect is in accordance with most literature findings about the effect of alkalis on cement setting. This is considered as an indication of alkalis presence in the extract. Most literature findings describe the acceleration of hydration as a distinct effect of alkalis in the aqueous solution (Jawed and Skalny, 1978; Salvador *et al.*, 2016). In the specific case though, no "flash setting" effect took place but an acceleration of 6.4% of initial setting. It is possible thought that other water-soluble elements were made available in the extract. This cannot be confirmed from the EDX spectra data of the present study.

#### **4.3.2.Alkali silica reaction test**

The results of the ASR test indicated a trend relating to the aggregate type in the mortar mix (Figure 9).

The reference mix with NA only, presented a distinct behaviour by being the only one that exhibited shrinkage. The mixes incorporating PC RA presented a trend of gradual length increase. Given the slope of the line it appeared that almost the same pace of length change was preserved during the test. Only the mix with 50% replacement of NA by PC RA presented a total length increase close to the limit in ASTM C1260-14 of 0.10%. For mixes with GPC RA, a trend of sharper length increase during the first week of immersion was observed. Both mixes exhibited a total length change significantly lower than that of the criterion, with PC\_25%GPC and PC\_50%GPC presenting values of 0.04% and 0.06% correspondingly.

This testing was to determine whether the recycled geopolymer aggregate itself could react and lead to ASR. It is recommended to use the accelerated mortar bar as a screening method especially for concrete RA (Gress *et al.*, 2000) therefore additional testing to determine whether

the additional alkalis introduced through the recycled geopolymers could result in ASR when combined with potentially reactive aggregates will be conducted.

#### **4.3.3. Compressive strength testing**

The compressive strength test of all mixes indicates that the incorporation of GPC RA resulted to a strength reduction (Figure 10). It appeared that the mix with 25% PC RA had the highest strength of all mixes, followed by the mix with 25% GPC RA. It is remarkable that all mixes, with the exception of PC\_50%GPC, presented 28-day strength values higher than the reference mix. In the case of recycled aggregate concrete or mortar, the final strength is dependent on numerous parameters, both physical and chemical (Pepe *et al.*, 2014; Tam *et al.*, 2009). One of the most distinct characteristic of recycled aggregates, their high water absorption, can affect the nominal water to cement ratio and therefore the final strength (Malešev *et al.*, 2010; P. De Pauw, 1998; Kwan *et al.*, 2012). In the specific case, it appeared that for mortars with the same replacement levels, the incorporation of GPC RA resulted to lower values compared to PC RA. This could be related to the chemical composition of the RA material but also the workability of the mix as the mixes used here had a constant water content. As mentioned in literature, the presence of alkalis in the mortar leads to lower strength at later ages (Mota Gassó, 2015; Jawed and Skalny, 1978).

#### **5. Conclusions**

In this study, SEM/EDX elemental mapping coupled with leaching tests proved to be a valid approach for investigation of alkalis migration from recycled geopolymer concrete. Research findings showed that incorporation of GPC RA in mortars could increase the alkalinity of the mix through two distinctive mechanisms.

- (i) Alkalis solubility in water: The sharp increase of leachate alkalinity demonstrated that there is a short window, during and after mixing, in which the unbound alkalis become available in the aqueous phase. As a consequence the chemistry of the mixing water and the paste is altered.
- (ii) Alkalis migration through the paste-aggregate interface: The findings indicate that Na migration can occur through the interface, by  $\text{Ca}^{2+}$  and  $\text{Na}^{+}$  exchange between the two

materials. Elemental mapping coupled with EDX spectra showed higher Na concentrations close to the paste- aggregate interface than in the rest of the paste. The corresponding Ca maps indicated transport from the PC paste into the GPC RA.

BSE/SEM images revealed a complex paste-aggregate interfacial transition zone (ITZ), while formation of additional calcium-silicon based phases in the geopolymeric matrix was identified by EDX spectra.

GPC incorporation resulted on minor effects on PC mortar properties susceptible to presence of additional alkalis in the mix.

GPC RA leachate accelerated initial setting time of PC paste by 13 minutes. However, further investigation is required to determine its chemical composition.

All mixes with the exception of PC\_50%GPC demonstrated higher compressive strength than the reference mix. The results do not show distinct effect of GPC on the strength but this is also dependent on mix design parameters or age of testing. GPC RA demonstrated an effect comparable to that of PC RA.

The screening test for ASR indicated that GPC RA did not show tendency to expand or indicate ASR any more than recycled PC aggregates. More complex systems taking into account the action of potentially reactive aggregates are to be investigated.

This research contributes into developing a fundamental understanding of the mechanisms and effects of alkali transport on behaviour of recycled geopolymer concrete. No detrimental effects were observed on PC mortars due to GPC RA incorporation, implying this recycling practice is feasible. However, further investigation of more complex systems is required.

## **6. Acknowledgements**

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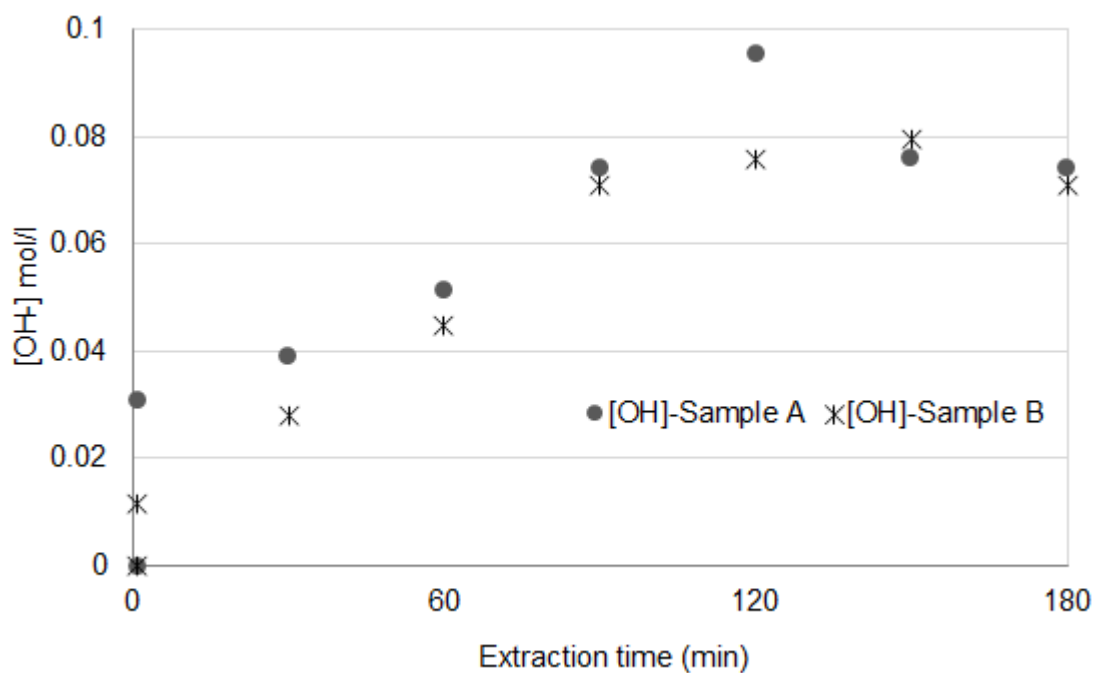
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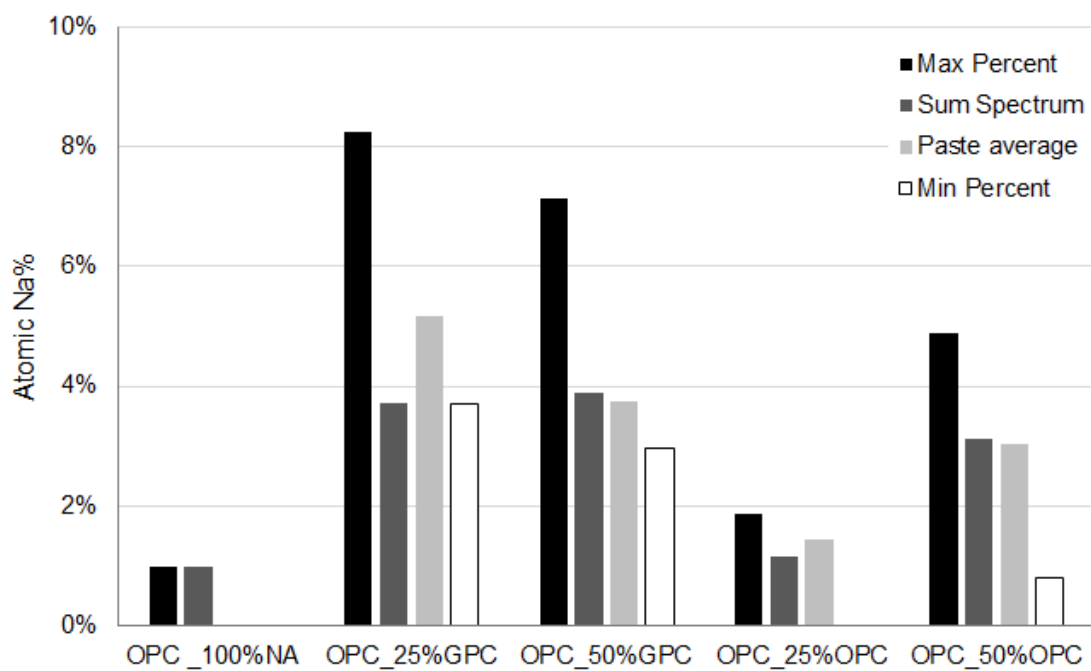
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## 8. Figure captions

505 Figure 1 OH<sup>-</sup> concentration of water GPC RA extract as calculated from pH measurements



506  
507 Figure 2 Measured atomic Na % of PC mortars according to EDX spectra from elemental  
508 mapping



509

Figure 3 PC\_50%GPC Site 1 a) BSE SEM image of polished sample with the ITZ border drawn  
b) Elemental map of calcium (Ca) c) Elemental map of sodium (Na)

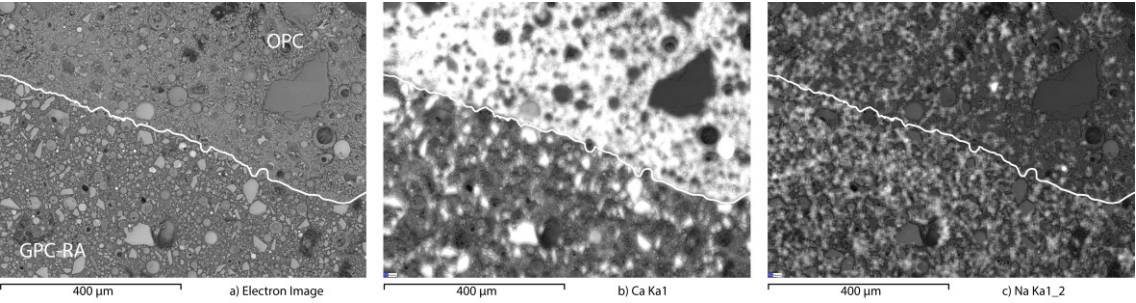


Figure 4 PC\_50%GPC Site 2 a) BSE SEM image of polished sample with the ITZ border drawn  
b) Elemental map of calcium (Ca) c) Elemental map of sodium (Na)

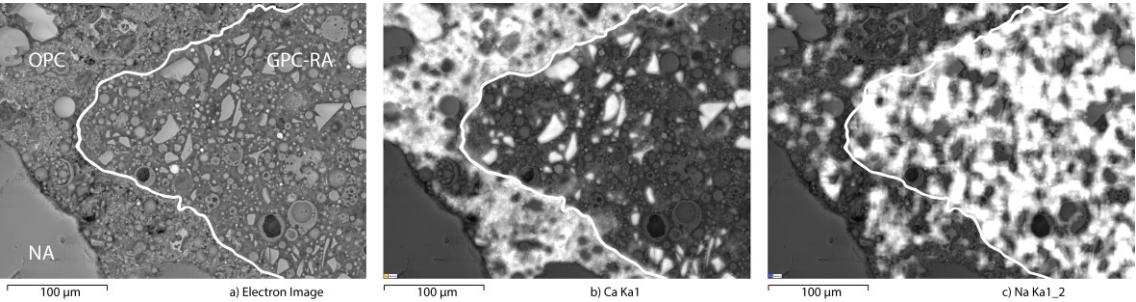


Figure 5 PC\_25%GPC Site 1 a) BSE SEM image of polished sample with the ITZ border drawn  
b) Elemental map of calcium (Ca) c) Elemental map of sodium (Na)

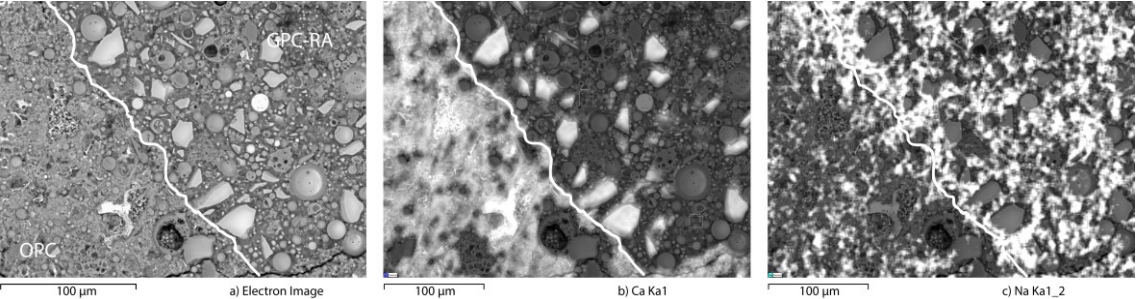


Figure 6 PC\_50%GPC Site 3 a) BSE SEM image of polished sample with the ITZ border drawn  
b) Elemental map of calcium (Ca) c) Elemental map of sodium (Na)

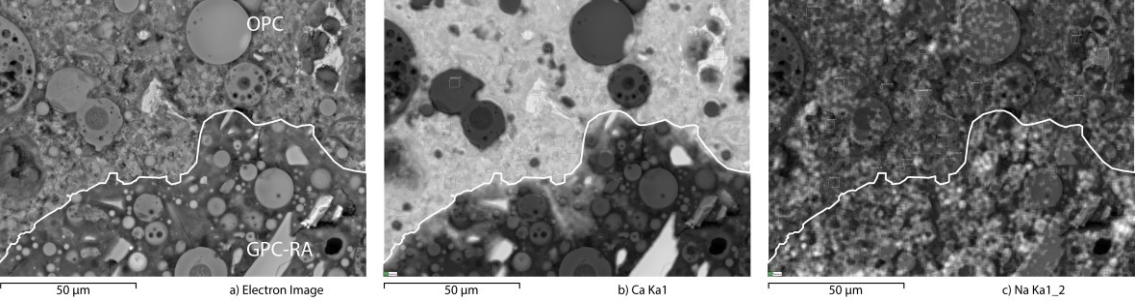




Figure 7 PC\_25%GPC Site 2 a) BSE SEM image of polished sample with the ITZ border drawn  
b) Elemental map of calcium (Ca) c) Elemental map of sodium (Na)

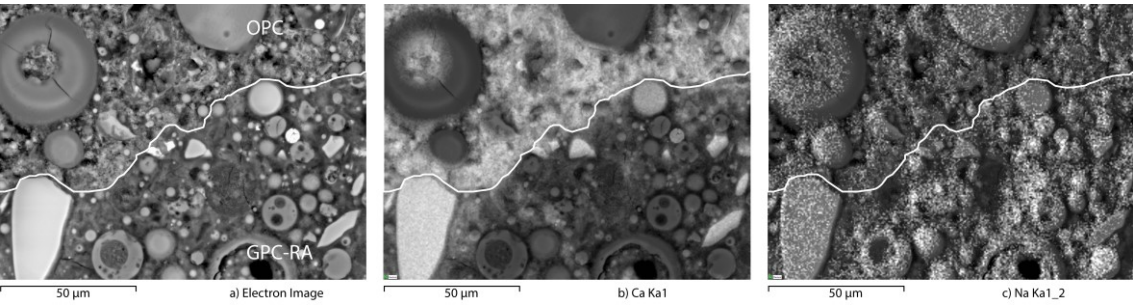


Figure 8 Average of atomic Na % from EDX spectra on points of interest at the paste, interfacial transition zone (ITZ) and geopolymer aggregate (GPC RA) at samples PC\_25%GPC Site2 and PC\_50%GPC Site3

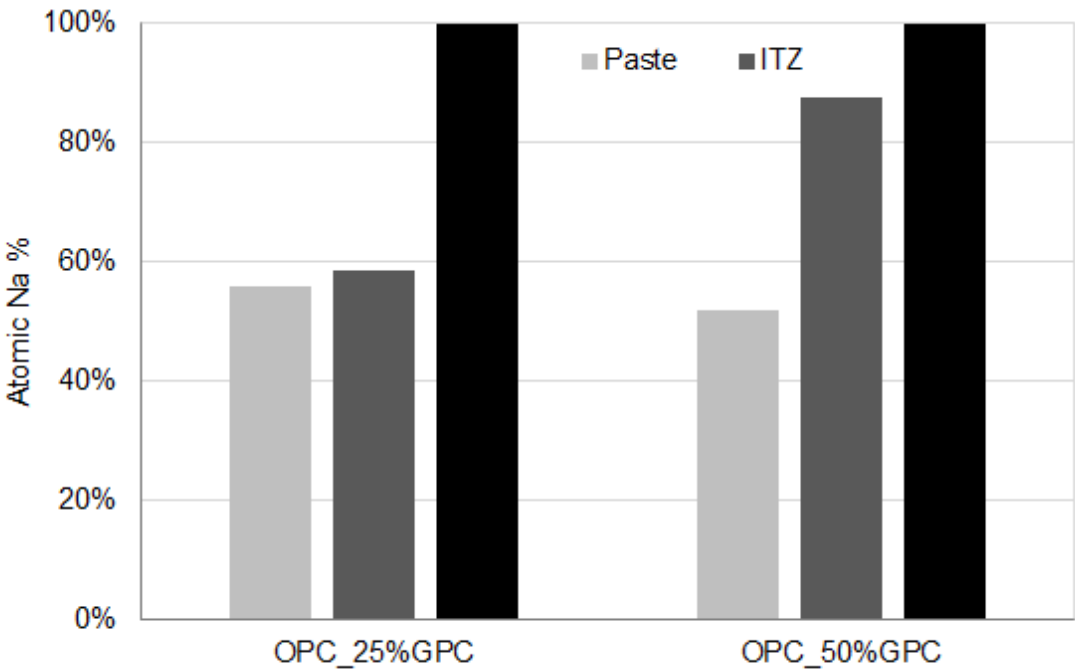


Figure 9. Mean % of length expansion for PC mortars after 14 days of H immersion in 1M NaOH solution for identifying ASR

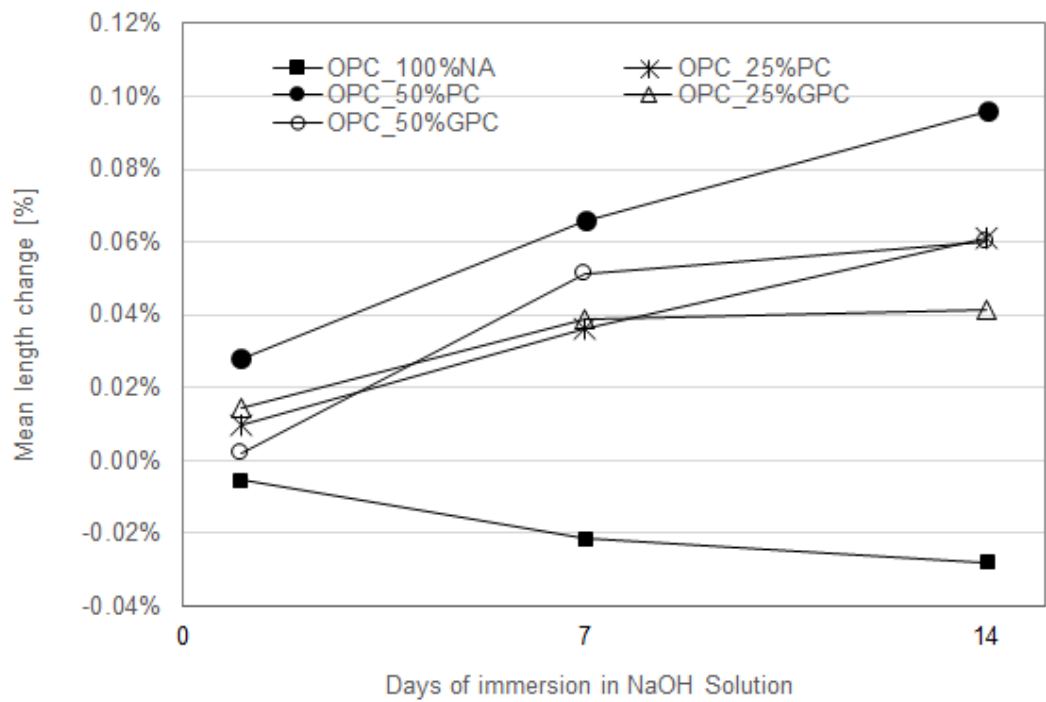
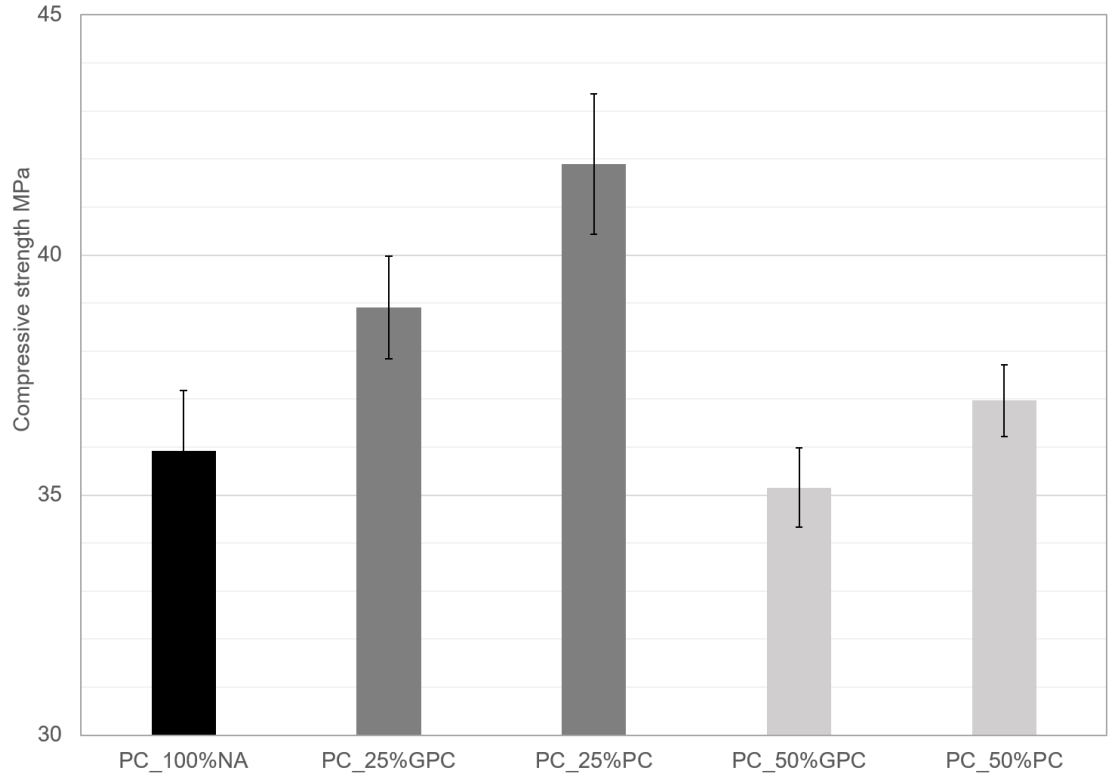


Figure 10 Compressive strength of mortars at 28 days



## 9. Table captions

Table 1 Mix design for mortars with recycled aggregates

Materials in kg/m <sup>3</sup>					
Sample ID	PC	NA	PC RA	GPC RA	Water
PC_100%NA	960	2160	-	-	451
PC_25%PC	960	1620	540	-	451
PC_50%PC	960	1080	1080	-	451
PC_25%GPC	960	1620	-	540	451
PC_50%GPC	960	1080	-	1080	451

536 Table 2 Chemical analysis of precursors by X-Ray fluorescence

Constituents (wt%)	GGBS	FA
SiO <sub>2</sub>	35.15	49
Al <sub>2</sub> O <sub>3</sub>	13.07	23.5
Fe <sub>2</sub> O <sub>3</sub>	0.28	8.7
CaO	39.6	2.4
MgO	8.47	1.4
SO <sub>3</sub>	0.17	0.8
Na <sub>2</sub> O	0.14	3.06
K <sub>2</sub> O	0.51	0.87
TiO <sub>2</sub>	0.66	
MnO	0.44	
P <sub>2</sub> O <sub>5</sub>		1.1
LOI	0.97	4.4

537